those of α Cygni was pointed out. Later, Mr. McClean* confirmed this, and further stated that the bright lines of η Argus corresponded with the dark lines of the Nova; while later still, Sir David Gill† has shown the similarity between the spectra of η Argus and Nova Aurigæ. Hence we are led to the conclusion that the temperatures reached in the outbursts of both these Novæ were not greatly different from those of the stars named, and that in η Argus there are constant conditions which are similar to those temporary conditions which produce the appearance of Novæ.

In the table the lines of Nova Persei are compared with those recorded by Campbell‡ and Vogel§ in Nova Aurigæ.

The probably corresponding lines of α Cygni, chromospheric lines, and enhanced lines, are also given in separate columns.

The reduction to wave-lengths and discussion of the lines in relation to those of other celestial and terrestrial spectra, has been undertaken by Mr. F. E. Baxandall, to whom my best thanks are due.

―――――――

"The Specific Volumes of Oxygen and Nitrogen Vapour at the Boiling-point of Oxygen." By JAMES DEWAR, M.A., D.Sc., LL.D., F.R.S.   Received January 21,—Read January 30, 1902.

In my paper on "The Boiling-point of Liquid Hydrogen determined by Hydrogen and Helium Gas Thermometers"‖ it was pointed out that a constant-volume gas-thermometer filled with oxygen gas, having a pressure at 0° C. of about 800 mm., gave a very accurate value of the boiling-point of liquid oxygen. As it seemed advisable to confirm this result indirectly, an attempt was made to determine the vapour density of oxygen at its boiling-point by direct weighing, the intention being, if the experimental results proved at all encouraging, to repeat the work on a larger scale and with greater precautions. As at present there is no likelihood of my being able to undertake the more accurate determinations, the results of the preliminary enquiry are presented to the Society. They give in any case, with considerable accuracy, the Specific Volumes which have never been directly determined.

In order to obviate any question of the buoyancy of the air, two flasks A and B of as nearly as possible the same air displacement were counterpoised on an Œrtling balance. The B flask remained per-

* 'M.N., R.A.S.,' vol. 61, p. 387.
† 'Roy. Soc. Proc.,' vol. 68, p. 457.
‡ 'Ast. and Ast. Phys.,' vol. 11, p. 808.
§ 'Ast. and Ast. Phys.,' vol. 12, p. 912.
‖ 'Roy. Soc. Proc.,' vol. 68, 1901.

manently on one scale of the balance during all the weighings, while the A flask was weighed, either exhausted or filled with oxygen (or nitrogen), under various circumstances according as the experiments required.

As the flask cooled in the liquid oxygen or air had to stand an internal pressure of from three to four atmospheres, it was considered expedient to select a spherical vessel of about 300 c.c. capacity, to which was sealed a narrow tube having a very carefully ground stop-cock at its end. Preliminary experiments were made to determine the change of volume of the flask when subjected to internal pressure. The flask, filled with air at five atmospheres pressure, was left for 24 hours with the stopcock closed, without showing any leakage. To determine the effect of pressure on the capacity of the flask, it was filled with water under one atmosphere pressure, and again with water under three to four atmospheres pressure (which included the range of the observations) and the weights noted. From these the coefficient of expansion of the flask was found to be 0·000306 per atmosphere excess of internal over external pressure. The temperature coefficient of expansion of glass (cubical) was taken to be 0·000025, which for a variation of temperature of some 200° altered the capacity of the flask by about 1·5 c.c. The content of the flask up to a fixed mark on the neck below the stopcock was determined to be 315·973 c.c. at 17° C. ; the content between the mark and the stopcock was determined both by measurement and by the weight of mercury it contained, and was found to be 0·127 c.c.

Before each experiment the A flask filled with the gas under observation was exhausted to a pressure of from 2 to 4 mm. of mercury (which was afterwards involved as a correction in reducing the observations) and weighed, the weight *a* which had to be added to its scale pan to balance the B flask being noted. The A flask was then filled with carefully purified oxygen (or nitrogen), and the temperature of the flask and contents (still in communication with the gas reservoir) was lowered by immersing it up to the mark in liquid oxygen (or air) until the gas ceased passing into the flask, and the pressure was finally equalised to that of the atmosphere. This is really the most important part of the manipulation, as the accuracy mainly depends on giving sufficient time to the cooling, while at the same time taking care to avoid any excess of pressure that would necessarily. lead to liquid condensation on the glass surface. During the rapid inrush of gas, it is advisable to keep the pressure well below that of the barometer at the time, and to finally adjust the pressure at the end of the absorption. The vessel containing the liquid oxygen had a cardboard cover which crossed the neck of the flask at the mark, thereby preventing the cooled vapour of the oxygen from freezing the stopcock. The remaining portion of the tube between the mark and the stopcock, namely,

0·127 c.c., was therefore approximately at the temperature of the room. When the temperature of the flask and its contents became stationary the stopcock was closed, the flask removed, and after heating up to the temperature of the room, weighed against the B flask and any further necessary counterpoise b. The weight of oxygen vapour in the flask at its boiling-point was thus equal to $a + b$, subject to the corrections which have been indicated.

To the five sources of error or correction indicated above, there remains to be added that due to additional buoyancy of the air during the weighing of the flask, when filled with oxygen at its boiling-point, for these weighings were made at the temperature of the room, which would cause a rise of pressure in the flask and therefore expansion of its volume. But this error was so small that it could safely be neglected.

As the intention was not only to ascertain the density of oxygen and nitrogen at their respective boiling-points under atmospheric pressure, but also under diminished pressure, experiments were made with nitrogen at ordinary temperatures and at pressures varying from about one-sixth of an atmosphere to ordinary pressures, in order to find the range of variation in the results with the 316 c.c. flask to be used in the subsequent low-temperature experiments. In the following table are details of these observations, and the results reduced according to the ordinary gaseous laws.

Table I.—Density of Nitrogen, ordinary Temperature.

No.	p_1.	T_1.	p.	a.	b.	V.	d.	d_0.
	mm.	°	mm.	gramme	gramme			
1	742·0	15·5	742·0	0·37	−0·0022	315·973	0·001168	0·001265
2	742·0	15·5	742·0	0·3668	−0·001	315·973	0·001162	0·001258
3	742·0	16·0	742·0	0·367	−0·0015	315·973	0·001161	0·001259
4	751·0	16·5	281·3	0·371	−0·2328	315·913	0·000442	0·001265
5	751·0	16·5	284·2	0·371	−0·231	315·913	0·000447	0·001269
6	751·0	17·0	268·5	0·371	−0·239	315·911	0·000422	0·001269
7	753·0	17·5	176·2	0·3705	−0·2850	315·899	0·000275	0·001262

where p_1 = barometric pressure at the time of observation,

T_1 = temperature of the room at the time of observation,

p = pressure of the nitrogen vapour in the flask during the experiment,

a, b = as defined before,

V = the volume of the flask corrected for temperature and compression,

d = the calculated density at T_1° and pressure p,

d_0 = the value of d reduced to 0° and 760 mm. by the ordinary gaseous laws.

In reducing these observations the following corrections were involved : a correction of 0·0015 gramme, due to imperfect exhaustion of the flask A while being weighed as empty ; the correction due to the neck of the flask between the mark and the stopcock was negligible ; the volume of the flask when corrected for temperature was 315·973 c.c., and when it was necessary to correct further for excess of external over internal pressure, the values were as given in Column V ; in the last four experiments this correction varied from about 0·059 to 0·073 c.c.

The first three experiments give a mean value of 1·260 grammes, at standard temperature and pressure, as the weight of a litre of nitrogen. This is about a quarter per cent. higher than the accepted value of 1·257. The extreme variation in the individual experiments is about half a per cent. The average value of the results under about one-third of an atmosphere is 1·266 grammes ; the tendency under the low pressures being to make the density half a per cent. higher. Considering that in the actual low-temperature experiments the mass of gas to be weighed would be at least three times greater, it was inferred that in spite of difficulties of manipulation and corrections the results might be anticipated to lie within a half per cent. of the true value.

The following table gives the results of six experiments made on the density of the vapour of oxygen at its boiling-point taken as 90°·5

Table II.—Density of Oxygen Vapour at its Boiling-point.

No.	$p = p_1$.	T_1.	a.	b.	d.	v.
	mm.	°	gramme.	gramme.		
1	775 ·5	15 ·5	0 ·388	1 ·0225	0 ·004402	227 ·15
2	770 ·3	16 ·5	0 ·3865	1 ·015	0 ·004403	227 ·07
3	771 ·0	17 ·5	0 ·3875	1 ·0245	0 ·004432	225 ·60
4	771 ·8	17 ·5	0 ·3875	1 ·0260	0 ·004432	225 ·59
5	775 ·0	16 ·0	0 ·388	1 ·028	0 ·004422	226 ·12
6	774 ·2	16 ·5	0 ·3875	1 ·028	0 ·004425	225 ·97

absolute, and under atmospheric pressure, where p, p_1, T_1, a, b, are the same symbols as used in the previous table, d is the calculated density at 90°·5 absolute and 760 mm., and v is the specific volume $1/d$.

In the above reductions the following corrections were involved : 0·002 gramme due to imperfect exhaustion of A flask while being weighed as empty; 0·0002 gramme due to the contents of the neck of the flask between the mark and the stopcock not being at 90°·5 ; the volume of the flask up to the mark contracted at 90°·5 to 314·398 c.c. ; no correction was necessary for compression.

Thus the mean weight of one litre of oxygen vapour at 760 mm. and 90°·5 absolute is 4·420 grammes, and the specific volume is

2 C 2

226·25 c.c.   If the first two experiments are eliminated on the assumption that the proper equilibrium of temperature had not been attained, the average weight per litre would become 4·428 grammes, and the specific volume 225·82.

Taking Regnault's density of oxygen at 0° and 760 mm., the density at 90°·5 in the ordinary way would be 0·0043137, and the specific volume 231·82 c.c.   Thus the volume given by the ordinary gaseous laws is 1·0246 times the average observed volume ; or we may put it that pv is diminished at the boiling-point of oxygen by 2·46 per cent. Again, while the ratio of the absolute temperatures is 3·017, the ratio of the densities is 3·091.

Behn* has determined by an indirect method the specific volume of oxygen, and finds the value 358, which is nearly 60 per cent. greater than the volume found by the direct method.   The mode of procedure he adopts is to ascertain directly three quantities out of four in the ordinary thermodynamic equation correlating latent heat, temperature, increment of pressure to temperature, and specific volume, thereby deducing the unknown quantity.   Now of the three experimental values required, one, viz., increment of pressure to temperature, can only be got by calculation from the vapour-pressure curve, and much depends upon the accuracy of this value.   Accepting Estreicher's vapour pressures for liquid oxygen below its boiling-point as the most reliable, a Gibbs equation gives the increment per degree near 740 mm. pressure as 78·67 mm. mercury pressure or 106·93 grammes per square centimetre.   This value, taken along with the latent heat found by Behn, and the boiling-point, gives, when inserted in the thermodynamic equation, a specific volume of 223·55, which is within less than 2 per cent. of the value found by the direct-density determinations.†

Further experiments were made on oxygen vapour at 90°·5 and under reduced pressures.   These experiments and their results are given in the following table.   The same symbols are used as in the preceding tables, except that d is the calculated density at 90°·5 absolute and pressure p, and v is $1/d$.   The corrected volume of the flask is entered under V.

---

* 'Ann. der Physik,' vol. 1, 1900, "Sublimationswärme der Kohlensäure und die Verdampfungswärme der Luft."

† In the same way Behn's specific volume of carbonic acid would be contradictory of my proof that a constant-volume gas-thermometer filled with carbonic acid at about atmospheric pressure gives a very accurate value of its own boiling-point. Assuming the ordinary gaseous laws, the specific volume ought to be 361·6 instead of 423 given by Behn.   Now my value of the increment of pressure to temperature at the boiling-point is 62·84 mm. mercury pressure, and this, along with the values used by Behn in the thermodynamic equation, gives 363 as the specific volume. This comes much nearer the anticipated value of the constant.

Table III.—Density of Oxygen Vapour at its Boiling-point under
Diminished Pressure.

No.	p_1.	T_1.	p.	a.	b.	V.	d.	v.
	mm.	°	mm.	gramme	gramme			
1	741·8	18·5	287·0	0·3695	0·1315	314·340	0·001588	625·74
2	741·8	18·5	281·5	0·3695	0·1345	314·339	0·001607	622·01
3	746·5	20·0	279·0	0·3690	0·1290	314·338	0·001588	629·41
4	746·5	20·0	310·2	0·3690	0·1880	314·342	0·001776	562·95
5	746·5	19·0	159·4	0·3690	0·0850	314·323	0·000907	1101·46

In reducing these observations the following corrections were involved : a correction of 0·0014 gramme to 0·0015 gramme due to imperfect exhaustion of the A flask while being weighed as empty ; the correction due to the neck of the flask between the mark and the stopcock not being at 90°·5 amounted to 0·00003, 0·00007 gramme and was practically negligible ; the volume of the flask, which, when corrected for temperature, was 314·398 c.c., had to be further corrected for excess of external pressure over internal pressure by amounts varying from 0·0551 c.c. to 0·0742 c.c. If the first three experiments are averaged (the pressures being so near), the weight of a litre of oxygen at 90°·5 absolute under a pressure of 282·5 mm. would be 1·5982 grammes. The ratio of this density to the value previously found for one atmosphere pressure, viz., 4·42 grammes, is 2·765, and the ratio of the pressures is 2·690. It appears that the ratio of the change of density of the vapour of oxygen at 90°·5 absolute, under variable pressure, is greater than the ratio of the change of pressure. It is clear, however, that it would be necessary to work upon a larger scale in order to get satisfactory vapour densities at low temperatures under pressures below that of the atmosphere.

The following table gives the observations on the density of nitrogen vapour at the boiling-points of liquid oxygen and liquid air respectively ; the first two were made in oxygen, the last four in air. The symbols used are the same as before, except that d is the calculated density at T° absolute and 760 mm. and v is $1/d$.

Table IV.—Density of Nitrogen Vapour at the Boiling-point of
Oxygen.

No.	$p = p_1$.	T_1.	a.	b.	d.	v.	T.
	mm.	°	gramme.	gramme.			°
1	771·8	17·5	0·3875	0·8555	0·0039021	256·27	(90·5)
2	773·0	17·0	0·385	0·8555	0·003885	257·39	(90·5)
3	777·2	16·0	0·3885	0·9575	0·004192	238·53	84·05
4	777·3	16·5	0·3885	0·9500	0·004168	239·90	84·54
5	777·3	16·5	0·3885	0·942	0·004143	241·34	85·04
6	777·3	16·5	0·3845	0·9235	0·004073	245·49	86·50

In reducing these observations, the following corrections were involved : a correction of 0·002 gramme due to imperfect exhaustion of the A flask, while being weighed as empty ; the correction due to the neck of the flask between the mark and the stopcock not being at temperature T amounted to 0·00014 gramme and was practically negligible ; the volume of the flask, which only required to be corrected for temperature, was 314·398 c.c.

Experiments 1, 2 were made with liquid oxygen taken to be at temperature 90°·5 absolute. The experiments 3, 4, 5, 6 were made in one and the same sample of liquid air, with rising temperature. For these temperatures, obviously only a few degrees below the boiling-point of oxygen, the ordinary gaseous laws may be held to apply, in order to determine their values. Thus we may employ the formula

$$T = v\,\frac{90\cdot5}{256\cdot833},$$

where 256·833 is the mean of the volumes of Nos. 1, 2, to get the temperature of the last four experiments. The values thence obtained are entered in column T.

The first two experiments made with liquid oxygen give a ratio of the nitrogen densities from my own values of 3·088, the absolute temperature ratio being 3·017 ; my values for the ratio of the oxygen densities for the same range of temperature being 3·091 as previously deduced. We may safely assume that if the density of nitrogen were observed at its boiling-point it would deviate as much from the ordinary gaseous laws as oxygen. Further, the specific volume of nitrogen at its boiling-point of 78° absolute, would from the above formula be 221·3 as compared with 226·2, the similar value found for oxygen.

The general inference to be drawn from these preliminary experiments is that reliable vapour densities may be determined at very low temperatures. There seems to be no reason why the vapour density of hydrogen at its boiling-point should not be accurately ascertained ; only, as in this case the internal pressure in the weighing flask would amount to nearly 15 atmospheres, it would be advisable to construct the flask of some metal or alloy. A flask of the size used in the oxygen experiments filled with the vapour of hydrogen at its boiling-point would be equivalent in weight to between 4 and 5 litres of hydrogen at the ordinary temperature and pressure, and such an amount of material ought to give density results at the boiling-point of hydrogen of considerable exactness, notwithstanding the great manipulative difficulties that would necessarily be involved in the execution of such a determination at 21° absolute.